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(19) (CA) **APPLICATION FOR CANADIAN PATENT** (12)

(54) Stabilizer for Chlorine-Containing Polymers

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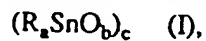
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Stabilizer for chlorine-containing polymers

Abstract of the disclosure

A stabilizer composition for chlorine-containing polymers and chlorine-containing polymer compositions, comprising

a) at least one organotin oxide compound of the formula



where R is C₁-C₁₈alkyl; a is the number 1 or 2; b = (4-a)/2; and c is greater than or equal to 1; and

b) at least one perchlorate compound of a monovalent or divalent metal.

Polymer compositions of this type are preferably employed for external applications.

Stabilizer for chlorine-containing polymers

The invention relates to a novel stabilizer combination for chlorine-containing polymers, to a process for the stabilization of chlorine-containing polymers, to the chlorine-containing polymers obtainable in this way, and to the use of the stabilized polymers.

Organotin compounds, such as organotin alkoxides, carboxylates, mercaptides, oxides and sulfides, have been proposed a number of times as stabilizers or co-stabilizers for chlorine-containing polymers.

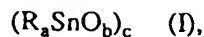
Organotin oxides are employed in combination with other compounds. US-A-3 196 129 and 3 919 165 disclose combinations with thiophosphates, acetals or phenols. Combinations with organotin mercaptides are described, for example, in DE-A-1 806 494.

The known stabilizers and stabilizer mixtures cannot meet all the demands made in the polymers. Thus, the very widely used organotin maleates, as preferred organotin carboxylates, cause a considerable tendency of the polymer melt to stick to the metal parts of the processing machines, which must be compensated by increased addition of lubricant. Other sulfur-free organotin compounds have a significantly worse thermostabilizing action than the maleates. Organotin oxides also exhibit this disadvantage, which becomes particularly noticeable during extrusion and injection moulding at elevated temperatures. Sulfur-containing organotin compounds frequently have an adverse effect on the light stability of the materials, which hinders use in outside applications.

The object was therefore to find a stabilizer system which enables the processing of chlorine-containing polymers at high temperatures and with high frictional stress. This preferably relates to processes such as extrusion and injection moulding.

Surprisingly, a stabilizer combination comprising an organotin oxide compound and a perchlorate compound of a monovalent or divalent metal meets the requirements to a large extent. In addition to good thermal stability and light stability, the mechanical properties of the chlorine-containing polymer are also favourably affected.

The invention therefore relates to a stabilizer composition comprising
a) at least one organotin oxide compound of the formula



where R is C₁-C₁₈alkyl; a is the number 1 or 2; b = (4-a)/2; and c is greater than or equal to 1; and

b) at least one perchlorate compound of a monovalent or divalent metal.

Components a) and b) can also be in the form of mixtures.

The novel stabilizer compositions may comprise further components. However, the novel stabilizer compositions preferably contain no further organotin compounds.

Suitable alkyl substituents having up to 18 carbon atoms are radicals such as methyl, ethyl, propyl, butyl, pentyl, hexyl, octyl, decyl, dodecyl, tetradecyl, hexadecyl and octadecyl, and corresponding branched isomers.

The chlorine-containing polymers can be those listed below: polymers of vinyl chloride, vinyl resins containing vinyl chloride units in their structure, such as copolymers of vinyl chloride and vinyl esters of aliphatic acids, in particular vinyl acetate, copolymers of vinyl chloride with esters of acrylic and methacrylic acid and with acrylonitrile, copolymers of vinyl chloride with diene compounds and unsaturated dicarboxylic acids or anhydrides thereof, such as copolymers of vinyl chloride with diethyl maleate, diethyl fumarate or maleic anhydride, post-chlorinated polymers and copolymers of vinyl chloride, copolymers of vinyl chloride and vinylidene chloride with unsaturated aldehydes, ketones and others, such as acrolein, crotonaldehyde, vinyl methyl ketone, vinyl methyl ether, vinyl isobutyl ether and similar; polymers of vinylidene chloride and copolymers thereof with vinyl chloride and other polymerizable compounds; polymers of vinyl chloroacetates and dichlorodivinyl ether; chlorinated polymers of vinyl acetate, chlorinated polymeric esters of acrylic acid and alpha-substituted acrylic acid; polymers of chlorinated styrenes, for example dichlorostyrene; chlorinated rubbers; chlorinated polymers of ethylene; polymers and post-chlorinated polymers of chlorobutadiene and copolymers thereof with vinyl chloride, rubber hydrochloride and chlorinated rubber hydrochloride; and mixtures of said polymers with one another or with other polymerizable compounds.

Also suitable are graft polymers of PVC with EVA, ABS and MBS. Preferred substrates are also mixtures of the abovementioned homopolymers and copolymers, in particular vinyl chloride homopolymers, with other thermoplastic and/or elastomeric polymers, in particular blends with ABS, MBS, NBR, SAN, EVA, CPE, MBAS, PMA, PMMA, EPDM and polylactones.

Also preferred are suspension, bulk and emulsion polymers.

The chlorine-containing polymer is particularly preferably polyvinyl chloride, especially a suspension polymer or bulk polymer.

Preference is given to stabilizer compositions as described above wherein a) is a compound of formula $(R_aSnO_b)_c$ (I), where R is C_4 - C_{12} alkyl; a is the number 1 or 2; $b = (4-a)/2$; and c is greater than or equal to 1. R is particularly preferably C_4 - or C_8 alkyl. Preference is also given to mixtures of compounds of the formulae R_2SnO (II) and $(RSnO)_2O$ (III), where R is C_1 - C_{18} alkyl, preferably C_4 - C_{12} alkyl. In the preferred mixtures of compounds of the formulae (II) and (III), the proportion of the compound of the formula (III) in the mixture does not exceed 20 % by weight.

Expedient stabilizer compositions are those as described above wherein b) is at least one perchlorate compound of monovalent metals, for example of alkali metals, including $LiClO_4$, $NaClO_4$ and $KClO_4$, or a perchlorate compound of divalent metals, for example metals from the 2nd main group or sub-group of the Periodic Table, such as $Zn(ClO_4)_2$, $Ca(ClO_4)_2$, $Sr(ClO_4)_2$, $Mg(ClO_4)_2$ and $Ba(ClO_4)_2$.

Component b) in the novel stabilizer compositions is preferably potassium perchlorate, sodium perchlorate, barium perchlorate, calcium perchlorate or magnesium perchlorate, or a mixture thereof.

Preferred stabilizer compositions comprise 70-95 % by weight of a compound of the formula (II), 0-10 % by weight of a compound of the formula (III) and 5-20 % by weight of a perchlorate compound of a monovalent or divalent metal, preferably an alkali perchlorate.

The present invention furthermore relates to stabilized chlorine-containing polymer compositions comprising a chlorine-containing polymer,

- a) at least one compound of the formula (I) and
- b) at least one perchlorate compound of a monovalent or divalent metal.

Preference is given to stabilized chlorine-containing polymer compositions comprising

- a) from 0.1 to 4 parts by weight of a compound of the formula (I),
- b) from 0.01 to 1 part by weight of a perchlorate compound of a monovalent or divalent

metal, and
100 parts by weight of chlorine-containing polymer.

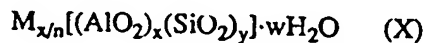
The preferred amount range for the compound of the formula (I) in the polymer composition is from 0.1 to 2.5 parts by weight, based on 100 parts by weight of chlorine-containing polymer. The preferred amount range for a mixture of the compounds of the formulae (II) and (III) in the polymer composition is from 0.1 to 2.5 parts by weight of a compound of the formula (II) and from 0 to 0.2 part by weight of a compound of the formula (III), in each case based on 100 parts by weight of chlorine-containing polymer.

The preferred amount range for the perchlorate compound of a monovalent or divalent metal in the polymer composition is from 0.05 to 1 part by weight, based on 100 parts by weight of chlorine-containing polymer.

A preferred stabilizer composition thus comprises, for example, 85 parts of $(C_8H_{17})_2SnO$, 2.5 parts of $(C_8H_{17}SnO)_2O$ and 12 parts of sodium perchlorate.

Preference is also given to stabilizer and polymer compositions which, in addition to a compound of the formula (I) and a perchlorate compound, also comprise a compound from the series consisting of crystalline alkali/alkaline earth metal aluminosilicates, preference being given to zeolites.

Zeolites can be described by the general formula (X)



in which n is the charge on the cation M;

M is an element from the first or second main group, such as Li, Na, K, Mg, Ca, Sr or Ba;

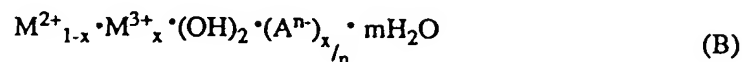
y:x is a number between 0.8 and 15, preferably between 0.8 and 1.2; and

w is a number between 0 and 300, preferably between 0.5 and 10.

Furthermore, zeolites which can be used are disclosed in "Atlas of Zeolite Structure Types", W.M. Meier and D.H. Olson, Butterworths, 3rd Edition, 1992.

Preference is also given to stabilizer and polymer compositions which, in addition to a compound of the formula (I) and a perchlorate compound, comprise a compound from the hydrotalcite series.

Compounds from the hydrotalcite series can be represented by the general formula (B)



where

M^{2+} = Mg, Ca, Sr, Ba, Zn, Cd, Pb, Sn and/or Ni,

M^{3+} = Al, B or Bi,

A^{n-} is an anion having the valency n,

n is a number from 1 to 4,

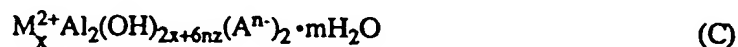
x is a number from 0 to 0.5, and

m is a number from 0 to 2.

A^{n-} is preferably OH^- , Cl^- , Br^- , I^- , ClO_4^- , HCO_3^- , CH_3COO^- , $C_6H_5COO^-$, CO_3^{2-} , SO_4^{2-} ,

$\begin{matrix} COO^- \\ | \\ COO^- \end{matrix}$, $(CHOHCOO)_2^{2-}$, $(CHOH)_4CH_2OHCOO^-$, $C_2H_4(COO)_2^{2-}$, $(CH_2COO)_2^{2-}$, $CH_3CHOHCOO^-$, SiO_3^{2-} , SiO_4^{4-} , $Fe(CN)_6^{3-}$, $Fe(CN)_6^{4-}$ or HPO_4^{2-} .

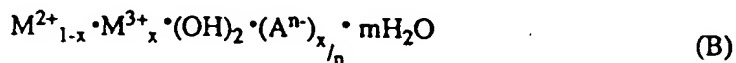
Other hydrotalcites which can expediently be employed are compounds of the general formula (C)



where M^{2+} is at least one metal from the series consisting of Mg and Zn, preferably Mg,

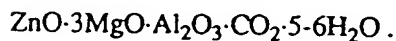
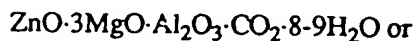
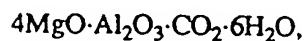
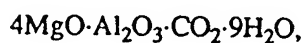
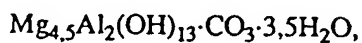
A^{n-} is an anion, for example from the series consisting of CO_3^{2-} , $\begin{pmatrix} COO^- \\ | \\ COO^- \end{pmatrix}^{2-}$, OH^- and S^{2-} , where n is the valency of the anion, m is a positive number, preferably from 0.5 to 5, and x and z are positive numbers, where x is preferably from 2 to 6 and z is less than 2.

Preference is given to compounds from the hydrotalcite series of the general formula (B)



where M^{2+} is Mg or a solid solution of Mg and Zn, A^{n-} is CO_3^{2-} , x is a number from 0 to 0.5, and m is a number from 0 to 2.

Very particular preference is given to hydrotalcites of the formulae



If further stabilizers from the series consisting of the organic and inorganic zinc, calcium, barium, magnesium and lead compounds, for example fatty acid salts, are used, it is possible to use, for example, from 0 to 10 parts by weight, based on the polymer composition. From 0.05 to 5 parts by weight, preferably from 0.1 to 5 parts by weight, are expedient.

The epoxide compounds which can be used for the purposes of the invention can have an aliphatic, aromatic, cycloaliphatic, araliphatic or heterocyclic structure; they contain epoxide groups as side groups. The epoxide groups are preferably bonded to the remainder of the molecule as glycidyl groups via ether or ester bonds, or they are N-glycidyl derivatives of heterocyclic amines, amides or imides. Epoxide compounds of these types are known in general terms and are commercially available.

The epoxide compounds contain at least one epoxy radical, in particular of the formula A



which is bonded directly to carbon, oxygen, nitrogen or sulfur atoms, where R_1 and R_3 are both hydrogen, R_2 is hydrogen or methyl, and n is 0, or in which R_1 and R_3 together are $-\text{CH}_2-\text{CH}_2-$ or $-\text{CH}_2-\text{CH}_2-\text{CH}_2-$, R_2 is then hydrogen, and n is 0 or 1.

Examples which may be mentioned of epoxide compounds are:

I) Glycidyl and β -methylglycidyl esters obtainable by reacting a compound containing at least one carboxyl group in the molecule and epichlorohydrin or glycerol dichlorohydrin or β -methylepichlorohydrin. The reaction is preferably carried out in the presence of bases.

The compounds containing at least one carboxyl group in the molecule can be aliphatic carboxylic acids. Examples of these carboxylic acids are glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, sebacic acid or dimerized or trimerized linoleic acid, acrylic acid, methacrylic acid, caproic acid, caprylic acid, lauric acid, myristic acid, palmitic acid, stearic acid and pelargonic acid.

However, it is also possible to employ cycloaliphatic carboxylic acids, for example cyclohexanecarboxylic acid, tetrahydrophthalic acid, 4-methyltetrahydrophthalic acid, hexahydrophthalic acid or 4-methylhexahydrophthalic acid.

It is also possible to use aromatic carboxylic acids, for example benzoic acid, phthalic acid, isophthalic acid, trimellitic acid or pyromellitic acid.

It is likewise possible to use carboxyl-terminated adducts, for example of trimellitic acid and polyols, for example glycerol or 2,2-bis(4-hydroxycyclohexyl)propane.

Other epoxide compounds which can be used for the purposes of the present invention are given in EP 0 506 617.

II) Glycidyl or β -methylglycidyl ethers obtainable by reacting a compound containing at least one free alcoholic hydroxyl group and/or phenolic hydroxyl group and a suitably substituted epichlorohydrin under alkaline conditions, or in the presence of an acid catalyst followed by alkali treatment.

Ethers of this type are derived, for example, from acyclic alcohols, such as ethylene glycol, diethylene glycol and higher poly(oxyethylene) glycols, propane-1,2-diol or poly(oxypropylene) glycols, propane-1,3-diol, butane-1,4-diol, poly(oxytetramethylene) glycols, pentane-1,5-diol, hexane-1,6-diol, hexane-2,4,6-triol, glycerol, 1,1,1-trimethylolpropane, bistrimethylolpropane, pentaerythritol, sorbitol, and from polyepichlorohydrins, butanol, amyl alcohol, pentanol and from monofunctional alcohols

such as isooctanol, 2-ethylhexanol, isodecanol and C₇-C₉alkanol and C₉-C₁₁alkanol mixtures.

However, they are also derived, for example, from cycloaliphatic alcohols, such as 1,3- or 1,4-dihydroxycyclohexane, bis(4-hydroxycyclohexyl)methane, 2,2-bis(4-hydroxycyclohexyl)propane or 1,1-bis(hydroxymethyl)cyclohex-3-ene, or they contain aromatic rings, such as N,N-bis(2-hydroxyethyl)aniline or p,p'-bis(2-hydroxyethylamino)diphenylmethane.

The epoxide compounds can also be derived from monocyclic phenols, for example from phenol, resorcinol or hydroquinone; or they are based on polycyclic phenols, for example on bis(4-hydroxyphenyl)methane, 2,2-bis(4-hydroxyphenyl)propane, 2,2-bis(3,5-dibromo-4-hydroxyphenyl)propane, 4,4'-dihydroxydiphenyl sulfone or on condensation products of phenols with formaldehyde obtained under acid conditions, such as phenol novolaks.

Examples of other possible terminal epoxides are: glycidyl 1-naphthyl ether, glycidyl 2-phenylphenyl ether, 2-biphenyl glycidyl ether, N-(2,3-epoxypropyl)phthalimide and 2,3-epoxypropyl 4-methoxyphenyl ether.

III) N-Glycidyl compounds obtainable by dehydrochlorinating the products of the reaction of epichlorohydrin with amines, which contain at least one amino hydrogen atom. These amines are, for example, aniline, N-methylaniline, toluidine, n-butylamine, bis(4-aminophenyl)methane, m-xylenediamine or bis(4-methylaminophenyl)methane, but also N,N,O-triglycidyl-m-aminophenol or N,N,O-triglycidyl-p-aminophenol.

However, the N-glycidyl compounds also include N,N'-di-, N,N',N''-tri- and N,N',N'',N'''-tetraglycidyl derivatives of cycloalkyleneureas, such as ethyleneurea or 1,3-propyleneurea, and N,N'-diglycidyl derivatives of hydantoins, such as of 5,5-dimethylhydantoin or glycol uril and triglycidyl isocyanurate.

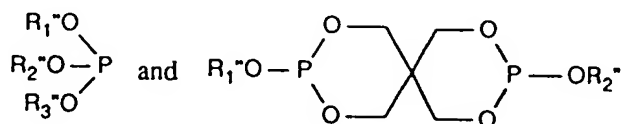
IV) S-Glycidyl compounds, for example di-S-glycidyl derivatives derived from dithiols, for example ethane-1,2-dithiol or bis(4-mercaptomethylphenyl) ether.

V) Epoxide compounds containing a radical of the formula A in which R₁ and R₃ together are -CH₂-CH₂-, and n is 0, are bis(2,3-epoxycyclopentyl) ether, 2,3-epoxycyclopentyl glycidyl ether or 1,2-bis(2,3-epoxycyclopentoxy)ethane. An example of an epoxy resin

containing a radical of the formula A in which R_1 and R_3 together are $-\text{CH}_2-\text{CH}_2-$ and n is 1 is (3',4'-epoxy-6'-methylcyclohexyl)methyl 3,4-epoxy-6-methylcyclohexanecarboxylate.

Other epoxy compounds which can be used, such as epoxidized soybean oil, are described, for example, in "Plastics Additives", editors H. Gächter and H. Müller, Hanser Verlag, 3rd edition, 1990, pages 303/4, and US 3 928 267.

The compositions according to the invention may also contain further stabilizers which are conventional for chlorine-containing thermoplastics. Thus, they contain, for example, 0-3 parts, in particular 0-1.5 parts, especially 0-1 part, based on the polymer composition, of one or more phosphites. Such phosphites can be used, for example, in an amount of 0.01-3 parts, in particular 0.01-1.5 parts, for example 0.01-1 part, preferably 0.1-0.6 part, for example 0.2-0.5 part. Examples of such phosphites are, for example, those of the formulae



in which R_1^* , R_2^* and R_3^* are identical or different and are $\text{C}_6\text{-C}_{18}$ alkyl, $\text{C}_6\text{-C}_{18}$ alkenyl, substituted or unsubstituted phenyl or $\text{C}_5\text{-C}_7$ cycloalkyl.

$\text{C}_6\text{-C}_{18}$ alkyl R_1^* , R_2^* and R_3^* are, for example, n-hexyl, n-octyl, n-nonyl, decyl, dodecyl, tetradecyl, hexadecyl or octadecyl. Preference is given to alkyl groups having 8 to 18 carbon atoms.

Substituted phenyl R_1^* , R_2^* and R_3^* are, for example, tolyl, ethylphenyl, xylyl, cumyl, cymyl, cresyl, 4-methoxyphenyl, 2,4-dimethoxyphenyl, ethoxyphenyl, butoxyphenyl, p-n-octylphenyl, p-n-nonylphenyl or p-n-dodecylphenyl.

Particularly suitable phosphites are trioctyl, tridecyl, tridodecyl, tritetradecyl, tristearyl, trioleyl, triphenyl, tricresyl, tris-p-nonylphenyl and tricyclohexyl phosphite and particular preference is given to aryl dialkyl phosphites and alkyl diaryl phosphites, for example phenyl didodecyl, 2,4-di-tert-butylphenyl didodecyl and 2,6-di-tert-butylphenyl didodecyl phosphite and dialkyl and diaryl pentaerythrityl diphosphites, such as distearyl pentaerythrityl diphosphite.

Preferred organic phosphites are distearyl pentaerythrityl diphosphite, trisnonylphenyl phosphite and phenyl didecyl phosphite.

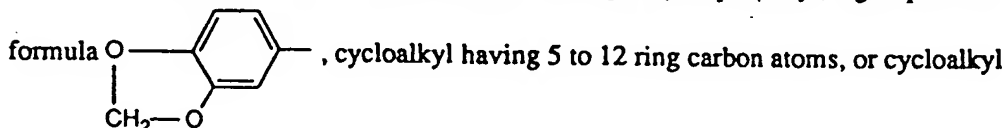
The compositions according to the invention may furthermore contain further known costabilizers, for example 0-2 parts, in particular 0-1.5 parts, based on the polymer composition. They are then preferably present in an amount of 0.01-2 parts, in particular 0.05-1.5 parts, for example 0.1-1 part, especially 0.1-0.5 part. Examples of these costabilizers which may be mentioned are 1,3-diketones, aminocrotonic esters, dehydracetic acid, 2,4-dihydroxybenzophenone, 2,4-dihydroxy-4'-tert-butylbenzophenone, dihydropyridine derivatives and pyrrole derivatives.

Expendient compounds are 1,3-diketones of the general formula (IV) or (IVa),



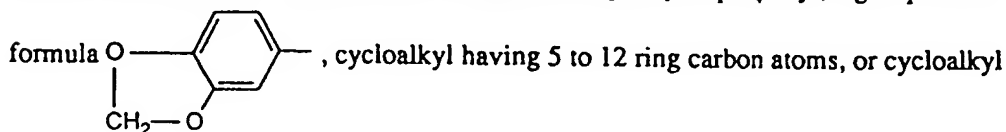
where

R^a is alkyl having 1 to 22 carbon atoms, C_5 - C_{10} hydroxyalkyl, alkenyl having 2 to 22 carbon atoms, phenyl, phenyl which is substituted by 1 to 3 groups in the series consisting of -OH, C_1 - C_4 alkyl, C_1 - C_4 alkoxy and halogen, or is phenyl- C_1 - C_4 alkyl, a group of the



having 5 to 12 ring carbon atoms which is substituted by 1 to 3 C_1 - C_4 alkyl groups,

R^c is alkyl having 1 to 22 carbon atoms, C_5 - C_{10} hydroxyalkyl, alkenyl having 2 to 22 carbon atoms, phenyl, phenyl which is substituted by 1 to 3 groups in the series consisting of -OH, C_1 - C_4 alkyl, C_1 - C_4 alkoxy and halogen, or is phenyl- C_1 - C_4 alkyl, a group of the



having 5 to 12 ring carbon atoms which is substituted by 1 to 3 C_1 - C_4 alkyl groups,

R^b is -H, alkyl having 1 to 18 carbon atoms, alkenyl having 2 to 12 carbon atoms, phenyl, C_1 - C_4 alkyl-substituted phenyl, phenyl- C_1 - C_4 alkyl, or a group of the formula $\begin{array}{c} -C-R^d \\ || \\ O \end{array}$,

where R^d is $-CH_3$, $-C_2H_5$ or phenyl, or in which

R^a and R^b together are a tetramethylene radical or a tetramethylene radical which is fused to a benzene radical, or

R^a and R^c together are a trimethylene radical or a trimethylene radical which is substituted by 1 to 3 C_1 - C_4 alkyl groups, and X is alkylene having 1-4 carbon atoms.

R^a and R^c as alkyl having 1 to 22 carbon atoms may be, for example, methyl, ethyl, propyl, n-butyl, tert-butyl, pentyl, hexyl, 2-ethylhexyl, nonyl, decyl, undecyl, dodecyl, tridecyl, octadecyl or eicosyl, and R^b as alkyl having 1 to 18 carbon atoms may be, for example, as defined above, apart from eicosyl.

Examples of C_5 - C_{10} hydroxyalkyl R^a and R^c are 5-hydroxypentyl, 6-hydroxyethyl and 7-hydroxyheptyl.

Examples of R^a and R^c as alkenyl having 2 to 22 carbon atoms are vinyl, propenyl, allyl, butenyl, methallyl, hexenyl, decenyl and heptadecenyl. Corresponding examples of R^b as alkenyl having 2 to 12 carbon atoms can be taken correspondingly from the above list.

The phenyl groups which are preferably substituted by one to three groups from the series consisting of -OH, C_1 - C_4 alkyl, C_1 - C_4 alkoxy and halogen, as mentioned for R^a and R^c , may be 4-hydroxyphenyl, 4-hydroxy-3,5-di- C_1 - C_4 alkylphenyl where C_1 - C_4 alkyl is, for example, methyl or t-butyl, or methylphenyl, dimethylphenyl, ethylphenyl, n-butylphenyl, tert-butylphenyl, methyl-tert-butylphenyl, di-tert-butylphenyl, methoxy, ethoxyphenyl or monochlorophenyl.

C_1 - C_4 alkyl-substituted phenyl R^b is thus, for example, methylphenyl, ethylphenyl or tert-butylphenyl.

Phenyl- C_1 - C_4 alkyl R^a , R^b and R^c are, for example, benzyl or methylbenzyl.

R^a and R^c may also be cycloalkyl having 5 to 12 ring carbon atoms or cycloalkyl having 5 to 12 ring carbon atoms which is substituted by 1 to 3 C_1 - C_4 alkyl groups. Examples are cyclopentyl, cyclohexyl, cycloheptyl, cyclobutyl, cyclononyl, cyclododecyl, etc., and methylcyclohexyl, dimethylcyclohexyl, trimethylcyclohexyl and tert-butylcyclohexyl.

Examples of 1,3-diketones are: dehydracetic acid, dehydropropionylacetic acid, dehydrobenzoylacetic acid, cyclohexane-1,3-dione, dimedone, 2,2'-methylenebiscyclohexane-1,3-dione, 2-benzylcyclohexane-1,3-dione, acetyltetralone, palmitoyltetralone, stearoyltetralone, benzoyltetralone, 2-acetylcyclohexanone, 2-benzoylcyclohexanone, 2-acetylcyclohexane-1,3-dione, benzoyl-p-chlorobenzoylmethane, bis(4-methylbenzoyl)methane, bis(2-hydroxybenzoyl)methane, benzoylacetone, tribenzoylmethane, diacetylbenzoylmethane, stearoylbenzoylmethane, palmitoylbenzoylmethane, lauroylbenzoylmethane, dibenzoylmethane, 4-methoxybenzoylbenzoylmethane, bis(4-methoxybenzoyl)methane, bis(4-chlorobenzoyl)methane, bis(3,4-methylenedioxybenzoyl)methane, benzoylacetyloctylmethane, benzoylacetylphenylmethane, stearoyl-4-methoxybenzoylmethane, bis(4-t-butylbenzoyl)methane, butanoylacetone, heptanoylacetone, distearoylmethane, acetylacetone, stearoylacetone, palmitoylacetone, lauroylacetone, benzoylformylmethane, benzoylphenylacetylmethane, bis(cyclohexane-1,3-dionyl)methane and dipivaloylmethane.

1,3-Diketo compounds which can be used as costabilizers are in particular those described in DE-B 2 600 516 and EP-A 35 268, for example those of the formula given in the claim of DE-B 2 600 516. Preferred 1,3-diketo compounds are benzoylstearoylmethane, alkyl(for example ethyl) 2-benzoylacetoacetates and triacylmethanes.

Suitable aminocrotonic esters are, in particular, the esters with monohydric, straight-chain C_8 - C_{20} , in particular C_{12} - C_{18} alcohols, and/or with 1,3- or 1,4-butanediol and/or 1,2-dipropylene glycol and/or thiodiethylene glycol.

Pyrrole costabilizers which may be mentioned in particular are those described in EP-A 22 087 and GB-A 2 078 761, for example of the formula I given therein, preferably the pyrrole derivatives defined in Claims 2-9 of EP-A 22 087. An example which may be mentioned is 2-methyl-3-cyclohexyloxycarbonyl-4-phenyl-1H-pyrrole.

Other stabilizers which may be used in the compositions according to the invention are polyols. The amounts to be used are, for example, up to 3 parts by weight, expediently up to 2 parts by weight and preferably from 0.01 to 1 part by weight, based on 100 parts by weight of polymer composition. Typical examples of polyols are pentaerythritol, dipentaerythritol, trimethylolpropane, ditrimethylolpropane, tris(2-hydroxyethyl)

isocyanurate (THEIC), the latter being preferred, sorbitol, mannitol and inositol.

The compositions according to the invention may furthermore contain conventional antioxidants, pigments, light stabilizers and UV absorbers.

The present invention furthermore relates to a process for the stabilization of chlorine-containing polymers. To this end, in general the stabilizer composition comprising components a) and b) and, if desired, further additives is incorporated into the polymer, for which purpose equipment known per se, such as calenders, mixers, compounders and the like, can be used. Components a) and b) of the novel stabilizer composition and optional additives can also be added individually or in the form of a masterbatch to the polymers to be stabilized. Preferred components a) and b), preferred proportions and the other possible additives are evident from the above descriptions of the novel stabilizer and polymer compositions.

The compositions stabilized in accordance with the present invention can be converted into the desired shape by known methods. Such methods are, for example, calendering, extrusion, injection moulding or sintering, furthermore extrusion blow moulding or processing by the plastisol method. The compositions can also be converted into foams.

Preferred stabilized chlorine-containing polymer compositions are plasticizer-free or essentially plasticizer-free compositions.

The present invention furthermore relates to the use of the stabilized polymer compositions in particular, in the form of rigid formulations, for hollow articles (bottles), packaging films (thermoforming films), blown films, crash-pad films (automobiles), tubes, foams, heavy profiles (window frames), light-wall profiles, building profiles, sidings, fittings and equipment housings (computers and domestic appliances).

Other compositions, in the form of flexible formulations, are suitable for wire sheaths, cable insulations, decoration films, roof membranes, foams, agricultural sheeting, hoses, sealing profiles, office films and sheeting for inflated tents.

Examples of the use of the novel compositions as plastisols are artificial leather, flooring, textile coatings, wallcoverings, coil coatings and automotive underseal.

The above-described polymer compositions are preferably used as rigid PVC-based

materials for external applications and as rigid sheeting or thermoforming films for interior trim of motor vehicles.

The examples below illustrate the invention in greater detail. Parts and percentages are all by weight, unless stated otherwise.

Example 1: Various PVC compositions are prepared by mixing the individual components as shown in the table below (amounts in parts by weight).

Table 1:

| Example: | Comparison 1 | Comparison 2 | 1 |
|------------------------------|--------------|--------------|-------|
| S-PVC (K value 60) | 100.0 | 100.0 | 100.0 |
| Impact modifier (acrylate) | 6.0 | 6.0 | 6.0 |
| Wax ester | 1.2 | 1.2 | 1.2 |
| Dicarboxylate | 1.0 | 1.0 | 1.0 |
| Flow aid (acrylate-modified) | 1.0 | 1.0 | 1.0 |
| Di-n-octyltin oxide | 0.8 | --- | 0.8 |
| NaClO ₄ | --- | 0.07 | 0.07 |

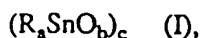
The PVC compositions are plasticated for 5 minutes at 190°C on mixing rolls. Test specimens are stamped out of the resultant film (thickness 0.2 mm) and heated in a Mathis Thermo-Takter oven at 190°C for the time shown in Table 2. The yellowness index (YI) is subsequently measured in accordance with ASTM 1925-70. The results in Table 2 below show a significant improvement in the stability for the sample according to the invention. A higher YI value indicates greater discoloration.

Table 2: YI of the test specimens after heating at 190°C

| | 0 | 10 | 20 | 30 | 40 | 50 [min] |
|--------------|------|------------------------------|-------|-------|---------------|----------|
| Comparison 1 | 84.4 | 87.9 | 111.5 | 136.1 | Decomposition | |
| Comparison 2 | >130 | Decomposition during rolling | | | | |
| Example 1 | 55.1 | 57.3 | 66.2 | 88.5 | 97.3 | 103.6 |

WHAT IS CLAIMED IS:

1. A stabilizer composition for chlorine-containing polymers, comprising
 - a) at least one organotin oxide compound of the formula



where R is C_1 - C_{18} alkyl; a is the number 1 or 2; $b = (4-a)/2$; and c is greater than or equal to 1; and

- b) at least one perchlorate compound of a monovalent or divalent metal.

2. A stabilizer composition according to claim 1, wherein component a) is a compound of the formula (I) in which R is C_4 - C_{12} alkyl.

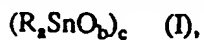
3. A stabilizer composition according to claim 1, wherein component a) is a mixture of compounds of the formulae R_2SnO (II) and $(RSnO)_2O$ (III) in which R is C_1 - C_{18} alkyl.

4. A stabilizer composition according to claim 1, wherein component b) is potassium perchlorate, sodium perchlorate, barium perchlorate, calcium perchlorate or magnesium perchlorate, or a mixture thereof.

5. A stabilizer composition according to claim 1, comprising
 - 70-95 % by weight of a compound of the formula (II),
 - 0-10 % by weight of a compound of the formula (III) and
 - 5-20 % by weight of a perchlorate compound of a monovalent or divalent metal.

6. A stabilized chlorine-containing polymer composition comprising a chlorine-containing polymer,

- a) from 0.1 to 4 parts by weight of at least one organotin oxide compound of the formula

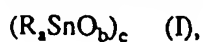


where R is C_1 - C_{18} alkyl; a is the number 1 or 2; $b = (4-a)/2$;

and c is greater than or equal to 1; and

- b) from 0.01 to 1 part by weight of at least one perchlorate compound of a monovalent or divalent metal.

7. A stabilized chlorine-containing polymer composition according to claim 6, comprising
 - a) from 0.1 to 4 parts by weight of at least one organotin oxide compound of the formula



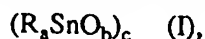
where R is C₁-C₁₈alkyl; a is the number 1 or 2; $b = (4-a)/2$;

and c is greater than or equal to 1;

b) from 0.01 to 1 part by weight of at least one perchlorate compound of a monovalent or divalent metal; and

100 parts by weight of chlorine-containing polymer.

8. A stabilized chlorine-containing polymer composition according to claim 6, comprising
a) from 0.1 to 2.5 parts by weight of at least one organotin oxide compound of the formula



where R is C₁-C₁₈alkyl; a is the number 1 or 2; $b = (4-a)/2$;

and c is greater than or equal to 1;

b) from 0.05 to 1 part by weight of at least one perchlorate compound of a monovalent or divalent metal; and

100 parts by weight of chlorine-containing polymer.

9. A stabilized chlorine-containing polymer composition according to claim 6, in which the chlorine-containing polymer is or comprises polyvinyl chloride.

10. A process for the stabilization of chlorine-containing polymers, which comprises adding

a) at least one organotin oxide compound of the formula



where R is C₁-C₁₈alkyl; a is the number 1 or 2; $b = (4-a)/2$;

and c is greater than or equal to 1; and

b) at least one perchlorate compound of a monovalent or divalent metal to the chlorine-containing polymer.

11. The use of a stabilized chlorine-containing polymer composition based on rigid PVC according to claim 6 as a material for external applications or as thermoforming sheeting.